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Radioactivity in Iberian Rivers with Uranium Mining Activities in their Catchment Areas

Fernando P. Carvalho[a]*, João M. Oliveira[a], Margarida Malta[a]

[a]*Instituto Superior Técnico/Laboratório de Protecção e Segurança Radiológica, Universidade de Lisboa, Estrada Nacional 10, km 139, 2695-066 Bobadela LRS, Portugal*

Abstract

Rivers flowing through the uranium mining region of Portugal, such as the Mondego and Zêzere rivers, receive drainage from areas of old uranium mines. The international River Águeda, a tributary to River Douro, has also important uranium mining and milling facilities in its catchment basin in Spain. In order to assess the radioactive contamination of these river basins resulting from uranium mining waste, uranium series radionuclides were measured in water, suspended particulate matter, and riverbed sediments. Results showed that significant radioactivity enhancement took place in sections of these rivers. This contamination persisted long time after environmental remediation implemented at some mine sites and cessation of mine discharges. The persistent risk of waste leaching and dam failure requires continued monitoring of radioactivity levels in these rivers.

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Keywords: Uranium mining; mine drainage; river sediments; radioactivity.

1. Introduction

The uranium mining industry in Portugal, mostly concentrated in the Centre North of the country, generated about 20 million tons of mining waste plus 5 million tons of milling tailings and sludge resulting from treatment of acid mine waters[1]. Most of uranium mining and milling waste materials were deposited on surface and have been exposed to weathering for many years. Following seasonal rains, surface runoff carrying leachates and particulate materials from these waste piles have the potential to cause enhancement of environment radioactivity levels and may reach streams

* Corresponding author. Tel.: 351-21-994 6332; fax: 351-21-955 0117.
E-mail address: carvalho@ctn.ist.utl.pt

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and main rivers. In the last few years, some of these uranium legacy sites, such as the Urgeiriça mine and milling site were remediated and radioactive waste was confined and covered with a multi-layer cap. The vital importance of river water for ecosystems health and sustained economic activities, such as agriculture and supply of drinking water for humans, requires proper industrial waste management and continuous environmental surveillance. Rivers flowing through the uranium mining region, namely the rivers Dão, Vouga, Távora, and the Mondego received water drainage from areas of old uranium mines during decades. Results on radioactivity assessment of these rivers were reported for 2006 [2]. The catchment areas of River Mondego and River Zezere with their main tributaries, plus the international River Águeda all receiving drainage from uranium mining areas were assessed on 2010 for radioactive contamination. Partial results of the radiological risk assessment for these river basins regarding uranium mine waste is reported herein.

2. Materials and Methods

There are several old uranium mines with large amounts of uranium wastes in the catchment basins of rivers Mondego, Zezere and Agueda (Figure 1). The main ones are Urgeiriça and Valinhos mines near the Ribeira da Pantanha stream, and Cunha Baixa and Quinta do Bispo mines near the Ribeira do Castelo. Both Pantanha and Castelo streams are tributaries to River Mondego. The mining and milling area of Urgeiriça was remediated and since 2007 at least, there are no discharges of untreated effluents into Ribeira da Pantanha. In the catchment of River Zêzere there are four main old mines, Vale de Arca, Carrasca, Pedreiros and Bica draining into the streams Valverdinho and Quarta-feira, which merge into Ribeira de Inguias - Ribeira de Caria, tributaries to River Zezere. The Iberian River Águeda has its source in Spain and receives drainage from uranium mines near Saelices el Chico, before becoming the border between the countries and joining the River Douro in Portugal.

Sampling was carried out in May 2010 in Mondego and Zezere basins. Results for the Águeda are from 1996-2000, and 2007, and were unreported. River water and bottom sediments were sampled at several locations in each river, including the tributaries referred to above. Water samples of about 10-15 L each were pressure filtered on site through 142 mm diameter, 0.45 µm pore size membrane filters, on Teflon coated filter systems. Filtered water was stored in polyethylene drums and acidified at pH<2 with HNO_3. Filters with suspended matter were folded, stored in identified plastic bags until analyses in the laboratory. Bottom sediment samples of the top 10 cm layer were collected using a hand operated sampler and stored in plastic boxes. In the laboratory, sediment samples were sieved and the small grain size sediment fraction <63 µm only was retained for analyses[3].

Isotopic tracers (^{232}U, ^{229}Th, ^{224}Ra, ^{209}Po, and 10 mg Pb^{2+}) were added to a measured volume of acidified filtered water samples of about 3 L for determination of the analytical chemical yield. Filters with suspended particulate matter (SPM) and sediment samples were also added known activities of isotopic tracers and dissolved in acids. Radioelements from samples were co precipitated, separated by radiochemical procedures, and electrodeposited onto stainless steel polished discs. Radionuclide measurements were made by alpha spectrometry using ion implanted silicon detectors (ORTEC EG&G). Analytical quality control of the results was ensured through periodic analysis of IAEA certified reference materials and participation in international radioanalytical intercomparison exercises[4,5].

3. Results and discussion

Activity concentrations of radionuclides in dissolved phase and suspended particulate matter (SPM) in streams Pantanha and Castelo, both receiving mine drainage, did show a clear enhancement of radioactivity from the drainage discharge points which lasted several km until joining the River Mondego. Just as an example, drainage from Quinta do Bispo mine released into the water stream contained still high uranium concentrations, determined at 1769 mBq/L of ^{238}U at station C6. This concentration was 60 times higher than the ^{238}U concentration measured upstream the discharge point, at C1, i.e., 26.8 mBq/L (Figure 1). The impact of this effluent discharge was measurable downstream, but faded with dilution in River Mondego. Similar enhanced concentrations of radionuclides from uranium series were determined in the soluble phase and SPM of streams receiving drainage in the catchment of the River Zêzere (not shown due to page limitations).

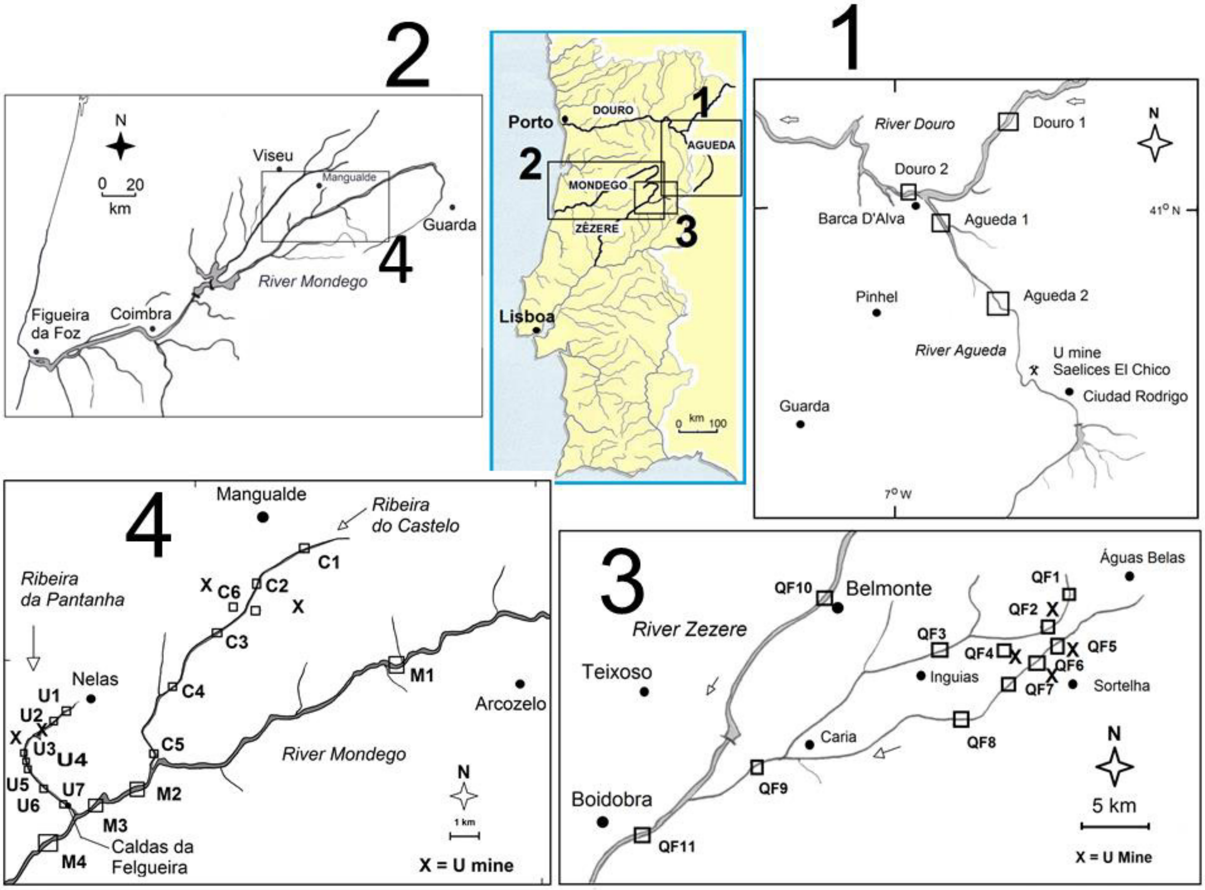

Figure 1. Location of the river basins investigated (top center) and blow-ups with sampling stations.1 River Águeda Basin; 2 River Mondego Basin; 3 Part of River Zêzere Basin; 4 Part of River Mondego Basin.

We will concentrate the discussion on results for river sediments because, although they may receive disturbance due to flash floods and agriculture works on the banks, they tend to be more stable integrators of contamination over the years. Activity concentrations of radionuclides in bottom sediments of River Mondego and its two tributaries, Ribeira da Pantanha and Ribeira do Castelo, are displayed in Table 1. In Ribeira da Pantanha, station U1, upstream the mine areas of Valinhos and Urgeiriça, was selected as a reference station. Radionuclide concentrations rose substantially in the area of Urgeiriça and gradually decreased downstream with the distance from mines. Sediments transported by Ribeira da Pantanha were generally high for all uranium series radionuclides even in the reference station U1 due to relatively high natural radioactive background of this uranium region. Contaminated stream sediments reached the River Mondego and enhanced concentrations in riverbed sediments downstream (M4) the discharge at Caldas da Felgueira. In the Ribeira do Castelo stream radionuclide concentrations increased with the discharges from mines Quinta do Bispo and Cunha Baixa and radioactivity enhancement was still measurable at C5, Póvoa de Luzianes, by the confluence with Mondego River (Table 1). Analyses of River Mondego samples collected upstream and downstream the junction of the two tributaries Castelo (M1, M2) and Pantanha (M3, M4) streams, showed an enhancement of radioactivity levels, although relatively small due to the important dilution of tributaries' discharges in this main river.

In the catchment area of River Zêzere, sediments of Ribeira de Quarta-feira, downstream Vale de Arca mine, showed a clear increase in radioactivity (#QF2) due to surface runoff of waste materials from the mine waste heaps (Table 2). Analyses of sedimentary materials near the water discharges of Carrasca (#QF4) and Bica (#QF7) mines confirmed that they were also sources of enhanced concentrations of uranium series radionuclides. Concentrations in the stream sediments decreased downstream in Ribeira de Inguias in the valley. Nevertheless, in the bottom sediments of Zêzere River at Boidobra (station#QF11), radionuclide levels were two times higher than at

Table 1. Radionuclide concentrations (Bq/kg dry weigh) in bottom sediments of River Mondego and tributaries.

Sampling location	Id.	^{238}U	^{235}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb=^{210}Po	^{232}Th
Ribeira da Pantanha	#U1	3872±103	189±8	3882±103	2192±80	829±76	506±18	277±15
Ribeira da Pantanha,Valinhos	#U2	4907±133	213±10	5212±141	2901±103	3696±276	2564±85	193±13
Barragem Nova, discharge	#U3	1876±53	89.4±5.2	1910±54	2549±89	3547±272	2471±79	123±9
Ribeira da Pantanha	#U5	5563±144	250±10	5285±137	3026±117	2223±187	2021±65	466±24
Ribeira da Pantanha	#U6	9118±242	395±15	9295±246	9523±324	2523±158	3425±127	693±30
Ribeira da Pantanha	#U7	8132±212	376±14	8324±217	10546±664	4014±429	3933±136	560±52
Ribeira do Castelo	#C1	548±16	25.2±2.0	568±17	186±7	325±24	438±15	108±5
Ribeira do Castelo	#C2	845±25	42.0±2.8	864±26	626±32	795±73	681±24	272±16
Ribeira do Castelo	#C3	1149±32	56.2±3.1	1149±33	852±27	534±35	630±21	241±9
Ribeira do Castelo	#C4	2946±82	126±6	2874±80	815±37	1544±151	728±25	203±13
Ribeira do Castelo	#C5	1080±31	54.4±3.2	1072±31	629±36	596±46	569±20	390±25
Quinta do Bispo, mine drainage	#C6	3009±81	130±6	2908±78	2099±68	1086±106	1429±47	122±8
Rio Mondego	#M1	383±13	15.9±1.7	375±13	378±13	411±34	310±13	301±11
Rio Mondego	#M2	539±16	23.4±1.8	558±16	412±14	273±31	446±17	317±12
Rio Mondego	#M3	396±12	17.4±1.6	398±12	365±16	467±71	290±11	236±12
Rio Mondego	#M4	1227±33	55.8±2.8	1237±34	1601±50	748±96	944±30	270±11

Table 2. Radionuclide concentrations (Bq/kg dry weigh) in bottom sediments of River Zêzere and tributaries

Sampling location	Id.	^{238}U	^{235}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb=^{210}Po	^{232}Th
Ribeira de Quarta-Feira	#QF1	727±21	33.2±2.4	724±21	530±20	582±38	599±20	130±7
Ribeira de Quarta-Feira	#QF2	3262±88	147±6	3274±88	1053±34	1022±50	1191±36	120±6
Ribeira de Quarta-Feira	#QF3	1142±34	51.4±3.6	1148±34	659±25	791±46	864±28	118±7
Carrasca Mine, drainage	#QF4	20584±879	934±53	20961±895	4654±149	4707±171	13683±680	65.5±6.7
Ribeira de Valverdinho	#QF5	746±22	34.6±2.3	758±22	779±26	446±35	640±21	189±8
Ribeira de Valverdinho	#QF7	4255±114	208±8	4269±114	1688±66	671±62	870±28	195±11
Ribeira de Valverdinho	#QF8	836±23	37.7±2.4	835±23	611±21	443±45	612±21	167±8
Ribeira das Enguias	#QF9	556±16	27.4±1.9	569±16	677±27	579±61	487±17	448±19
Rio Zêzere (Belmonte)	#QF10	254±9	10.8±1.1	252±9	282±14	160±31	237±8	143±8
Rio Zêzere (Boidobra)	#QF11	441±13	22.2±1.6	441±13	344±11	282±22	377±12	276±9

Table 3. Radionuclide concentrations in bottom sediments and water of River Águeda and River Douro.[6]

Sampling location	Id.	Sediments (Bq/kg dry wgt <75µm) (n=15)				Dissolved in water (mBq/L) (n=24)			
		^{238}U	^{235}U	^{234}U	^{226}Ra	^{238}U	^{235}U	^{234}U	^{226}Ra
River Águeda	#1	248±107	12±5	255±113	95±13	37.5±23.8	1.7±1.0	39.1±24.8	3.6±2.6
River Águeda	#2	140±44	7±2	143±44	76±6	35.3±19.4	1.7±0.9	36.6±19.9	5.1±8.8
River Douro	#1	81±24	4±2	81±24	116±52	23.5±14.0	1.2±0.7	24.7±11.8	4.5±7.1
River Douro	#2	127±57	6±3	128±63	93±34	32.6±3.6.5	1.6±1.8	35.6±30.5	3.8±3.5

Belmonte (#QF10). These results confirmed that radionuclides from the mine effluents were transported over the years and reached the River Zêzere, some 40 km far from the mines area.

In the River Águeda, concentrations of uranium and radium (^{226}Ra) in sediments and water are displayed in Table 3. These concentrations, averaged over five years, showed a decreasing trend both in uranium and radium along the Águeda and, after joining the Douro, showed also a decrease in radium concentration downstream Barca d' Alva[6]. Actually, the sediments transported by the River Águeda were lower in ^{226}Ra than those of River Douro. Drinking water for the public supply of Barca d'Alva is taken from a bore hole in the river bank. In 2007, a tailings dam failure in the uranium mine site at Saelices el Chico caused the discharge of large amounts of milling waste in the Águeda River. Measurements made in the River Agueda (#2) upstream Barca D´Alva, indicated that uranium concentration (U total) in river water jumped from about to 74 mBq/L to 360±8 mBq/L (i.e., 14 µgU/L) related to this accidental release, showing the vulnerability of the river system regarding uranium mine drainage. It should be pointed out that the maximum permissible concentration for uranium in drinking water is 15 µg/L [9,10].

4. Conclusions

The legacy of past uranium mining activities located in the catchment of rivers at center north of Portugal caused a radioactive impact in the environment. Waste heaps left uncovered for many years have been the source of radioactive materials that contributed to enhance radioactivity levels in rivers [7,8]. Due to recently improved water treatment stations for U mine effluents and the coverage of milling tailings at the Urgeiriça mine, radioactivity levels in the water and suspended particulate matter of Ribeira da Pantanha showed a decrease in comparison with previous years. Nonetheless, radioactivity in bottom sediments was still high and comparable to previous years, showing the persistence of radioactive contamination in riverbed sediments. Results showed also that radionuclides from the old uranium mines in the Sabugal County reached the River Zêzere. Radioactivity in the international River Águeda was elevated also with discharges from tailing dams in the uranium mine of Salices el Chico. In particular, a tailings' dam failure occurred in June 2007 released large amounts of radioactive materials into the Águeda and reached the River Douro. These results underscore that active uranium mines and legacy mine sites both require careful waste management and, often, treatment of waste water and mine water drainage. This radioactivity enhancement currently is not compromising the radiological quality of water stored in large artificial lakes built in these river systems. Nevertheless, the risk of waste leaching and waste dam failure, points out to the need for regular radioactivity monitoring and improved waste management, including environmental remediation of uranium sites to ensure radiation safety to the population and to the environment.

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